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MODELING THE EFFECT OF AGGLOMERATION IN NANOPARTICLE COOLANT SYSTEMS USING DYNAMIC LIGHT SCATTERING

INTERIM REPORT
TFLRF No. 420

by

Nigil Jeyashekar, Ph.D., P.E., James E. Johnson, Scott A. Hutzler, and Edwin A. Frame

U.S. Army TARDEC Fuels and Lubricants Research Facility
Southwest Research Institute® (SwRI®)
San Antonio, TX

for

U.S. Army TARDEC
Force Projection Technologies
Warren, Michigan

Contract No. W56HZV-09-C-0100 (WD0011)

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14. ABSTRACT
The objective of this research was to investigate nanofluids as new class of heat transfer fluids. Nanofluids were characterized using Dynamic Light Scattering (DLS) by obtaining volume fraction of aggregated nanoparticles as a function of aggregate radius. This data was used as an input to three analytical models to compute the overall thermal conductivity of the nanofluid. Stability analysis on alumina nanofluid (1% by vol.) indicated that the formation of aggregates was limited by diffusion and was primarily confined to the nanometer size range. A comparative study between dilute and regular alumina nanofluids concluded that the relationship between nanoparticle concentration and enhancement in thermal conductivity is nearly linear at both concentration regimes. Experiments on alumina nanofluids with 1% to 5% by volume concentration provided thermal conductivity enhancement up to 35%. This result concludes that aggregation of nanoparticles play a critical role in enhancement of thermal conductivity in nanofluids.

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Nanoparticle, Nanofluid, Dynamic Light Scattering, Thermal Conductivity

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EXECUTIVE SUMMARY

Fluids containing nanometer-sized particles, known as nanofluids, have shown to increase heat transfer potential. While significant research has been conducted with these fluids, a full understanding of the particle-to-particle energy transfer process has yet to be developed. With a better understanding of this process, fluid thermal systems with enhanced heat management capabilities can be developed. The objectives of this research was to investigate nanofluids as new class of heat transfer fluids. Analytical models that contain particle and base fluid properties are not sufficient for predicting effective thermal conductivity of the nanofluid. This is due to their inability to address the aggregation of nanoparticles dispersed in solution due to Brownian motion.

The Diffusion Limited Aggregation (DLA) process of nanoparticles in solution results in the formation of aggregates or nanoclusters. The focus of this research was to determine the contribution of nanoclusters to thermal conductivity of the base fluid. Nanofluid samples were prepared and analyzed using a technique called Dynamic Light Scattering (DLS) that provides volume fraction of nanoparticle clusters as a function of cluster radius. This data is used as an input to analytical models to compute the overall thermal conductivity of the nanofluid. The three models used in this research study were the Maxwell model, Fractal (Nanocluster) model, and modified Fractal (Nanocluster-Nanolayer) model. The Maxwell model was used to compute thermal conductivity of the nanofluid based on the total volume fraction, particle and base fluid thermal conductivities. The Fractal model takes agglomeration into account and uses data from the DLS experiments to compute the effective thermal conductivity. The modified Fractal model considers the formation of interfacial layers around each aggregate in addition to agglomeration. The thermal conductivities of the interfacial layers and aggregates are combined to evaluate the overall thermal conductivity of the nanofluid. All the DLS data for modeling work was provided by TARDEC.

Stability analysis that was conducted on alumina nanofluid (1.0 vol.%) has shown that the sizes of the aggregates were primarily confined to the nanometer size range. The microclusters that

were formed were highly unstable and had broken down to several nanoclusters. As the concentration was increased five times from dilute (0.2 vol.%) to regular (1.0 vol.%) nanofluid, the thermal conductivities also increased by approximately five times for all three thermal conductivity models. This result indicates that the near-linear relationship between particle concentration and thermal conductivity is preserved and is not affected by the aggregation of nanoparticles.

For 1.0% by volume nanofluid, based on the Maxwell model, the enhancement in thermal conductivity from the base fluid was estimated to be approximately 3%. However, for the same nanofluid, the enhancement in thermal conductivity due to aggregation predicted by Fractal model and modified Fractal model were 7.3 % and 7.5 % respectively. The result also indicates that the contribution of nanolayer to the overall thermal conductivity of the nanofluid is insignificant. For 0.2% and 1.0% by volume nanofluid solutions, the effect of aggregation (Fractal model) and nanolayer (modified Fractal model) increases the percentage enhancement in thermal conductivity by 2.5 times compared to the Maxwell model. As the particle concentration was increased to 5% by volume, the thermal conductivity was enhanced as high as 35%. This conclusion is important in highlighting the fact that nanoparticle aggregation plays a key role in enhancing the overall thermal conductivity of the nanofluid.

FOREWORD/ACKNOWLEDGMENTS

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ACRONYMS AND ABBREVIATIONS

%	Percent
°	Degree (Angle)
@	At
BZT	Benzethonium Chloride
DLCCA	Diffusion Limited Cluster-Cluster Aggregation
DLS	Dynamic Light Scattering
DI H_2O	De-ionized water
g	gram
K	Kelvin
Kg	Kilo-gram
L	Liter
Max	Maximum
Min	Minimum
ml	Milliliter
mol	Mole
mm	Millimeter
NIBS	Non-Invasive Back Scatter
nm	Nanometer
SEM	Scanning Electron Microscopy
SwRI	Southwest Research Institute
TCi	Thermal Conductivity Instrument
TARDEC	Tank Automotive Research, Development and Engineering Center
TFLRF	U.S. Army TARDEC Fuels and Lubricants Research Facility
W	Watt

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1.0 INTRODUCTION, OBJECTIVES AND TECHNICAL BACKGROUND

Coolants and cooling systems have been identified as important areas of research in ground vehicle science. Fundamental scientific research in this area has the potential to yield new technologies to enhance thermal efficiencies of vehicles. The management of heat flow is critical within an energy conversion process to maintain peak thermal efficiencies. For ground vehicles, more efficient means for conducting heat (fluid-metal interface) and rejecting heat to ambient air would yield better performing vehicles with potentially diminished impact on the environment. Fluids containing nanometer-sized particles, known as nanofluids, have shown increased heat transfer potential. While significant research has been conducted with these fluids, a full understanding of the particle-to-particle energy transfer process has yet to be developed. With a better understanding of this process, fluid thermal systems with enhanced heat management capabilities can be developed. RDECOM-TARDEC is conducting in-house research on nanofluids and Southwest Research Institute (SwRI) is a collaborator to support the research under Work Directive 11.

The overall objective of this research was to investigate nanofluids as new class of heat transfer fluids. The objective is accomplished by analyzing the experimental data in an effort to validate and compare the existing analytical models to predict thermal conductivity. TARDEC has used a new experimental approach called the Dynamic Light Scattering (DLS) technique to characterize nanofluid by measuring the volume fraction of nanoparticle aggregates as a function of particle size. This research provides new insights for explaining the physics of how nanometer-sized particles that are suspended in a carrier fluid has the potential to enhance thermal properties of the fluid. In this work directive, the analytical models used for estimating thermal conductivity addresses the aggregation of nanoparticles dispersed in solution to form nanoclusters. This information is critical to determine if the nanofluids thermal performance enhances or degrades with time in an engine or a similar heat transfer application. The experiments in this work directive primarily focused on analytical models that incorporates the DLA process, where the size of the nanoparticle aggregates from the DLS measurements was taken into account when calculating the overall thermal conductivity of the nanofluid.

As a collaborator to in-house research conducted by TARDEC, the objective of this work directive was to provide technical support by analyzing and modeling the experimental data, acquired in-house at TARDEC. The nanofluids were prepared by Oakland University and were sent to TARDEC for in-house experiments. TARDEC submitted the acquired data to SwRI for analysis and thermal conductivity modeling. All the data submitted to SwRI contained volume fraction of aggregates as a function of aggregate radius measured using the DLS technique. In Work Directive 11, three sets of data were sent to SwRI for analysis and modeling:

1. The first set of experiments was focused on stability of the nanofluid. The data set consists of DLS measurements obtained from 1 vol.% of alumina nanofluid at the rate of approximately 7 minutes, for a total time of 344 minutes. This aggregation data provides a window into the stability of the alumina nanofluid and the extent of variation of aggregate size over time.

2. The second set of experiments and data was a comparative study between 0.2 vol.% and 1.0 vol.% alumina nanofluid. The DLS data was used as an input to analytical models to compute thermal conductivity of the nanofluid and estimate the enhancement in thermal conductivity relative to the base fluid. The objective of this research was to determine if the relationship between computed thermal conductivity and particle volume fraction is linear in dilute (0.2 vol.%) and regular (1.0 vol.%) concentration regimes. These experiments also provide an insight to the enhancement in thermal conductivity when aggregation of particles is taken into account.

3. The third set of experiments investigated the relationship between computed thermal conductivity, based on analytical models and particle volume fraction. The objective of these experiments was to examine the rate of enhancement in thermal conductivity predicted by the analytical models with and without aggregation.

2.0 THERMAL CONDUCTIVITY MODELS AND DATA REDUCTION

In this work directive, three analytical models were used to compute the overall thermal conductivity of the nanofluid. The first analytical model is called the Maxwell model and was used to compute nanofluid thermal conductivity based on the assumption that nanoparticles are completely dispersed in the coolant (also referred to as base fluid). The second model, called the Wang or Fractal model computes the thermal conductivity of the nanofluid by taking into account the volume fraction and number of nanoclusters that resulted from Brownian motion of nanoparticles in the base fluid. The third model, called the modified Wang model or modified Fractal model, incorporates the effect of interfacial layer, also known as nanolayer, that were formed on the surface of nanoclusters to determine the overall thermal conductivity of the nanofluid. This model was developed at SwRI by combining the Wang model along with the nanolayer model. DLS data containing the volume fraction of nanoclusters and radius of nanoclusters was used as an input to all the three analytical models. This section provides a detailed description on fundamental formulation of the three analytical models that were used to compute the overall thermal conductivity of the nanofluid, based on DLS data from TARDEC's in-house experiments.

2.1 COMPLETE DISPERSION AND MAXWELL MODEL

A model for thermal conductivity of fluids in which small spheres are uniformly dispersed was formulated by James Maxwell (Maxwell, 1873). In the Maxwell model, the thermal conductivity of the nanofluid, k_{eff} (Equation 1) is based on the total particle volume fraction, φ, and thermal conductivities of particle, k_p, and base fluid, k_f.

$$\frac{k_{eff}}{k_f} = \frac{(1-\varphi) + 3\varphi \dfrac{k_p}{k_p + 2k_f}}{(1-\varphi) + 3\varphi \dfrac{k_f}{k_p + 2k_f}} \rightarrow (1)$$

In the above model, the thermal conductivity of the nanofluid increases linearly with particle volume fraction. For alumina nanoparticles that are completely dispersed in de-ionized water, the Maxwell model predicts that the thermal conductivity enhancement varies between 0.28 and

31.18 percent for particle volume fractions between 0.1 and 10 percent, at 20°C. However, comprehensive literature review of experimental and theoretical studies on alumina nanofluids have shown that thermal conductivity enhancements higher than that predicted by the Maxwell model (Özerinç *et al*., 2009). It was proposed that the increase in thermal conductivity is caused by the agglomeration of nanoparticles in the base fluid (Venerus and Jiang, 2011). Hence, there is a need to understand the agglomeration characteristics of nanoparticles in base fluids, and determine their impact on thermal conductivity. Also, there is limited experimental data on thermal conductivity of nanofluids below 1 percent by volume of nanoparticles and, at such low concentrations, nanofluids have shown anomalous increase in thermal conductivity (Choi, 2009). Thus, one of the tasks in this work directive was a comparative study between alumina nanofluids with 0.2 vol.% and 1 vol.%, in an effort to understand the relationship between particle concentration and thermal conductivity at dilute and regular nanoparticle concentration regimes.

2.2 FORMATION OF NANOCLUSTERS AND WANG (FRACTAL) MODEL

Nanoparticles that are dispersed in base fluid are in a constant state of random Brownian motion. For stationary nanofluid, this random motion of nanoparticles results in the formation of aggregates or clusters. The formation of aggregates depends on the short-range interparticle potential and sticking probability of either two particles, or particles and aggregates, or two aggregates (Prasher *et al*., 2006). The dynamics of irreversible aggregate formation could be either diffusion-limited or reaction-limited. Both aggregation mechanisms result in the formation of clusters of different radii (Weitz *et al*., 1985). At constant temperature, the Brownian velocity is inversely proportional to the square root of mass of nanoparticles and aggregates. The scale of size distribution governs diffusion of aggregates in the nanofluid and the sticking probability of particles and clusters. In the absence of convection, diffusion becomes the rate-limiting step leading to aggregate formation.

A model for the effective thermal conductivity of the nanofluid that accounts for agglomeration of spherical nanoparticles was developed by combining the effective medium approximation (Maxwell model) and the Fractal theory for description of nanoparticle aggregates or clusters

(Wang *et al*., 2003). The Fractal theory was developed based on the scale invariant nature of the aggregates or clusters. Equation 2 describes this Fractal model and takes into account the thermal conductivity of nanoparticle clusters (k_{cl}) and the number distribution of those clusters (n) as a function of cluster radius (r_{cl}). The effective thermal conductivity of the nanofluid in the Fractal model is determined by integrating the thermal conductivity of clusters and number of clusters.

$$\frac{k_{eff}}{k_f} = \frac{(1-\varphi) + 3\varphi \int_0^\infty \frac{k_{cl}(r_{cl}) \cdot n(r_{cl})}{k_{cl}(r_{cl}) + 2k_f} dr_{cl}}{(1-\varphi) + 3\varphi \int_0^\infty \frac{k_f . n(r_{cl})}{k_{cl}(r_{cl}) + 2k_f} dr_{cl}} \rightarrow (2)$$

The size of the nanoparticle aggregates or clusters are not exactly spherical, and r_{cl} refers to the radius of gyration of the aggregate. Equation 3 defines the number of clusters based on logarithmic-normal particle size distributions determined by dynamic light scattering, with the value of σ set to 1.5 and r_p representing the particle radius (Thomas, 1987).

$$n(r_{cl}) = \frac{1}{r_{cl}\sqrt{2}\pi \cdot \ln(\sigma)} \cdot exp\left\{ -\left[\frac{\ln\left({}^{r_{cl}}/_{r_p}\right)}{\sqrt{2}\pi . \ln(\sigma)} \right]^2 \right\} \rightarrow (3)$$

The thermal conductivity of nanoclusters can be predicted as a function of cluster size using the Bruggeman model (Bruggeman, 1935 and Wang *et al*., 2003). In equations 4 and 5, φ^* is the volume fraction of clusters of size r_{cl}, and is computed using the expression $\varphi^* = (r_{cl}/r_a)^{D-3}$, where D is the fractal dimension. For diffusion-limited cluster–cluster aggregation (DLCCA) mechanism of cluster formation, the fractal dimension (D) is determined to be 1.85 (Özerinç *et al*., 2009). Δ = Contribution to cluster thermal conductivity.

$$k_{cl} = (3\varphi^* - 1)k_p + [3(1-\varphi^*) - 1]k_f + \sqrt{\Delta} \rightarrow (4)$$

$$\Delta = (3\varphi^* - 1)^2 {k_p}^2 + [3(1-\varphi^*) - 1]^2 {k_f}^2 + 2[2 + 9\varphi^*(1-\varphi^*)]k_p k_f \rightarrow (5)$$

Based on the Fractal model, it can be concluded that the extent of agglomeration drives the size of nanoclusters. The volume fraction of nanoclusters in that size range has a direct bearing on the thermal conductivity of the nanofluid.

2.3 NANOCLUSTER-NANOLAYER AND MODIFIED WANG (FRACTAL) MODEL

In addition to nanoparticle agglomeration, the liquid molecules closer to the surface of nanoparticles form a nanolayer, which acts as a thermal bridge between a particle and the bulk liquid. Because of this, the thickness of the nanolayer could play an important role in thermal conductivity enhancement of the nanofluid. The Structural model of nanofluids is considered to consist of solid nanoparticle cluster, bulk liquid, and a nanolayer surrounding the particle (Yu and Choi, 2003). The thermal conductivity equation based on the Fractal model is modified to account for total nanolayer thickness, radius of the cluster, and thermal resistance of the interfacial layer in the region between the particle and the bulk fluid (Xie *et al*., 2005). Figure 1 shows a representative sketch of an aggregate of size, r_{cl} with thermal conductivity, k_{cl}, surrounded by an interfacial layer of thickness δ.

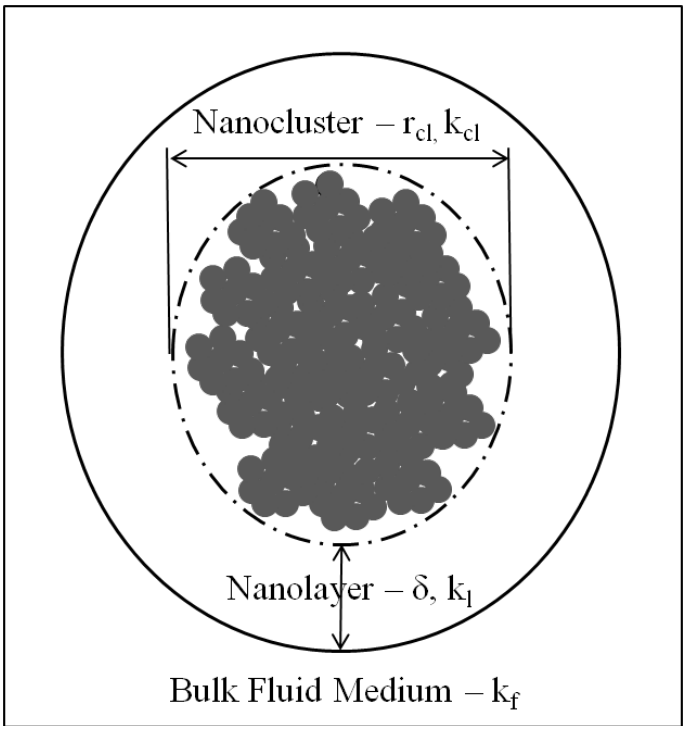

Figure 1. Structural Model of Nanoclusters, Nanolayer, and the Bulk Fluid Medium

The complexity of the physiochemical interactions are avoided by assuming that the thermal conductivity of the interfacial layer, $k(r)$, varies linearly from the surface of the nanoclusters to the bulk fluid, where $r_{cl} \leq r \leq r_{cl}+\delta$. The modified thermal conductivity distribution, $k(r)$, inside the nanolayer is shown by Equation 6 and the modified thermal resistance, R_{layer}, of the interfacial layer is shown by Equation 7. The thickness of the nanolayer in Equation 8 is dependent on the properties of the base fluid and is not affected by the new Structural model. The thermal conductivity of the interfacial layer, k_l, is shown by Equation 9. M_f is the molecular weight, and ρ_f is the density of the base fluid. N_A denotes the Avogadro's constant. Equations 6–9 were proposed by Xie *et al*. (2005).

$$k(r) = \left[\frac{k_f - k_{cl}}{\delta}\right] \cdot r_{cl} + \left[\frac{k_{cl} \cdot (r_{cl} + \delta) - k_f \cdot r_{cl}}{\delta}\right] \rightarrow (6)$$

$$R_{layer} = \int_{r_{cl}}^{r_{cl}+\delta} \frac{dr}{4\pi r^2 k(r)} \rightarrow (7)$$

$$\delta = \frac{1}{\sqrt{3}} \cdot \left[\frac{4M_f}{\rho_f N_A}\right]^{1/3} \rightarrow (8)$$

$$k_l(r_{cl}) = \frac{\delta}{r_{cl} \cdot (r_{cl} + \delta) \cdot [4\pi R_{layer}]} \rightarrow (9)$$

The thermal conductivity of the aggregate (Equations 4 and 5) can be modified to include the thermal conductivity of the interfacial layer. This modification is done by replacing k_p in Equations 4 and 5 with k_{cp}, as shown in Equation 10 (Özerinç *et al*., 2009).

$$k_{cp} = k_l \frac{(k_p + 2k_l) + 2A^3(k_p - k_l)}{(k_p + 2k_l) - A^3(k_p - k_l)} \rightarrow (10)$$

$$A = 1 - \frac{\delta}{\delta + r_p} \rightarrow (11)$$

In Equations 2, 4, and 5, (r_p+t), $[(r_p+t)/r_p]^3\varphi$ and k_{cp} should be substituted for r_p, φ, and k_p, respectively, when both agglomeration and interfacial layer are used to account for effective thermal conductivity of the nanofluid.

3.0 EXPERIMENTAL METHODS

3.1 DYNAMIC LIGHT SCATTERING MEASUREMENTS

The effect of nanoparticle agglomeration and nanolayer structure on thermal conductivity of the nanofluid can be investigated using the DLS technique to provide data on volume fraction of clusters as a function of cluster radius. DLS measurements are performed using the Zetasizer Nano Series® instrument and 0.5 ml of the representative nanofluid sample. The instrument performs size measurements based on the Brownian motion of aggregates, and relates it to the size of the particles. The particles are illuminated with a monochromatic laser light. The intensity fluctuations in the scattered light are analyzed for volume and number distributions of nanoparticle clusters. The Zetasizer Nano System measures the rate of intensity fluctuations due to movement of aggregates and calculates the size of the aggregates. The fundamental size distribution generated is an intensity distribution and is converted using the Mie theory to a volume distribution. The Zetasizer instrument is programmed to provide an output containing volume distribution as a function of nanoparticle cluster radius. The Non-Invasive Back Scatter (NIBS) technique is used to obtain the volume fraction-size distributions.

The process by which data was collected is shown in Figure 2. The NIBS technique is defined by the angle at which the detector collects the scattered light. For the NIBS technique, the back scatter angle is 173°. The helium neon laser (1), with a wavelength of 632.8 nm, is passed through an attenuator (2) to reduce the beam intensity, prior to sample illumination (3). The detector (4) is positioned at 173° to collect the scattered light. The volume distribution, size data is obtained from the Zetasizer instrument software, after signal processing and correlation by the digital signal processor (correlator) (5).

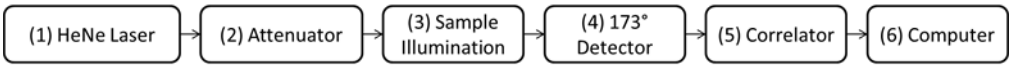

Figure 2. Non-Invasive Backscatter DLS Measurement

3.2 NANOFLUID SAMPLES

The nanofluids samples were prepared for TARDEC by Oakland University. This report focuses on properties of the nanofluid samples. In summary, the nanofluid samples were prepared by dispersing the nanoparticles in the base fluid followed by sonication at a specific power level for a specified duration. The nanofluid preparation and properties will be provided to TARDEC by Oakland University. These details are beyond the scope of this report. The nanofluid samples have been issued the following labels and the experiments associated with them are listed below:

1. FL-13973-11 – This was a 1.0 vol.% alumina nanofluid and was used analyzing the stability of the nanofluid over a period of 344 minutes.

2. FL-13973-11 and FL-13971-11 - These were 1.0 vol.% alumina nanofluids, also called regular nanofluids, prepared on different dates. A portion of these two samples were used to obtain a 0.2 vol.% nanofluid sample by dilution. The regular nanofluid samples were labeled as FL-13973-11-ND and FL-13971-11-ND and the dilute nanofluids were labeled as FL-13973-11-D and FL-13971-11-D.

3. FL-14193-11, FL-14194-11, FL-14195-11, FL-14196-11, and FL-14197-11 were samples with particle concentrations from 1-5 vol.%. These samples were used to study the effect of increasing concentration of nanoparticles coupled with agglomeration on overall thermal conductivity of the nanofluid.

4.0 STABILITY ANALYSIS OF NANOFLUIDS

The regular nanofluid with 1.0 vol.% nanoparticle concentration was analyzed for aggregation for 344 minutes. Figure 3 shows the mean and range of volume fraction of aggregates as a function of aggregate radii during the entire time of DLS measurements. It should be noted that the diffusion process drives aggregation into the microclusters range as indicated in Figure 4.

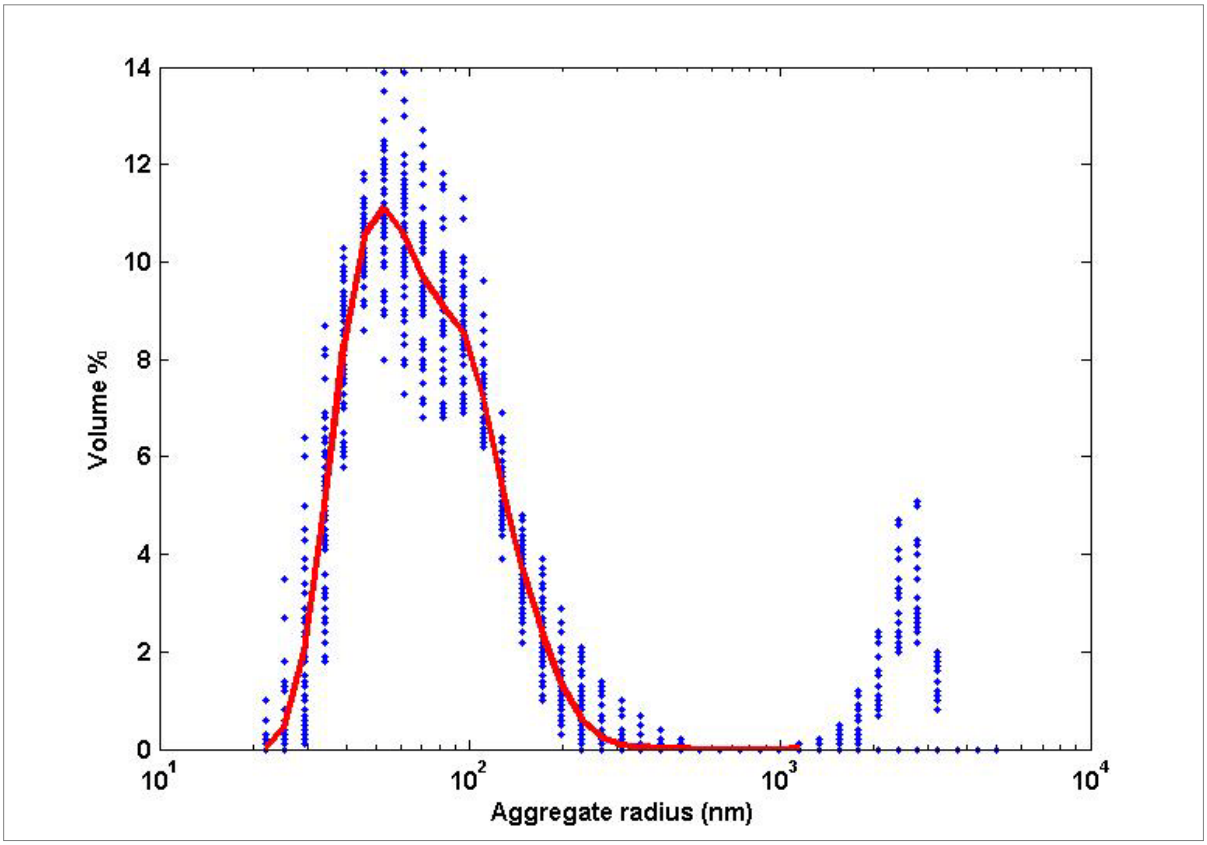

Figure 3. Mean and Range of Volume Fraction of Aggregates

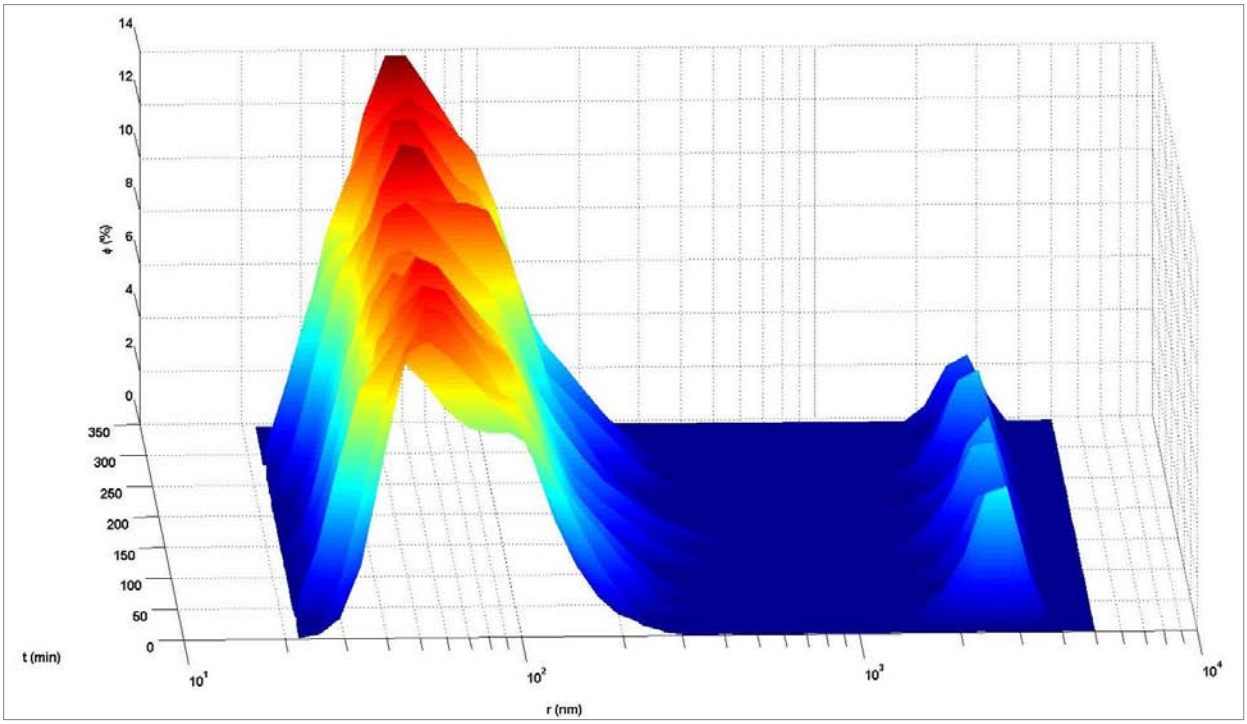

Figure 4. Three Dimensional Chart of Aggregate Volume Fraction

The stability of the microclusters that resulted from the diffusion limited aggregation process was determined based on the color map of aggregates shown in Figure 5. Diffusion of nanoparticles and aggregates drives the formation of microclusters in the size range 10^3-10^4 nm. However, these microaggregates were unstable as they were not present during the entire time that the data was acquired. The largest volume fraction of microclusters formed during the first one hour of measurements and were present at lower concentrations from 75-300 minutes followed by insignificant cluster formation after 340 minutes. Based on the data, it can be concluded that nanoparticle formation is primarily confined to a radius of 20 to 500 nm.

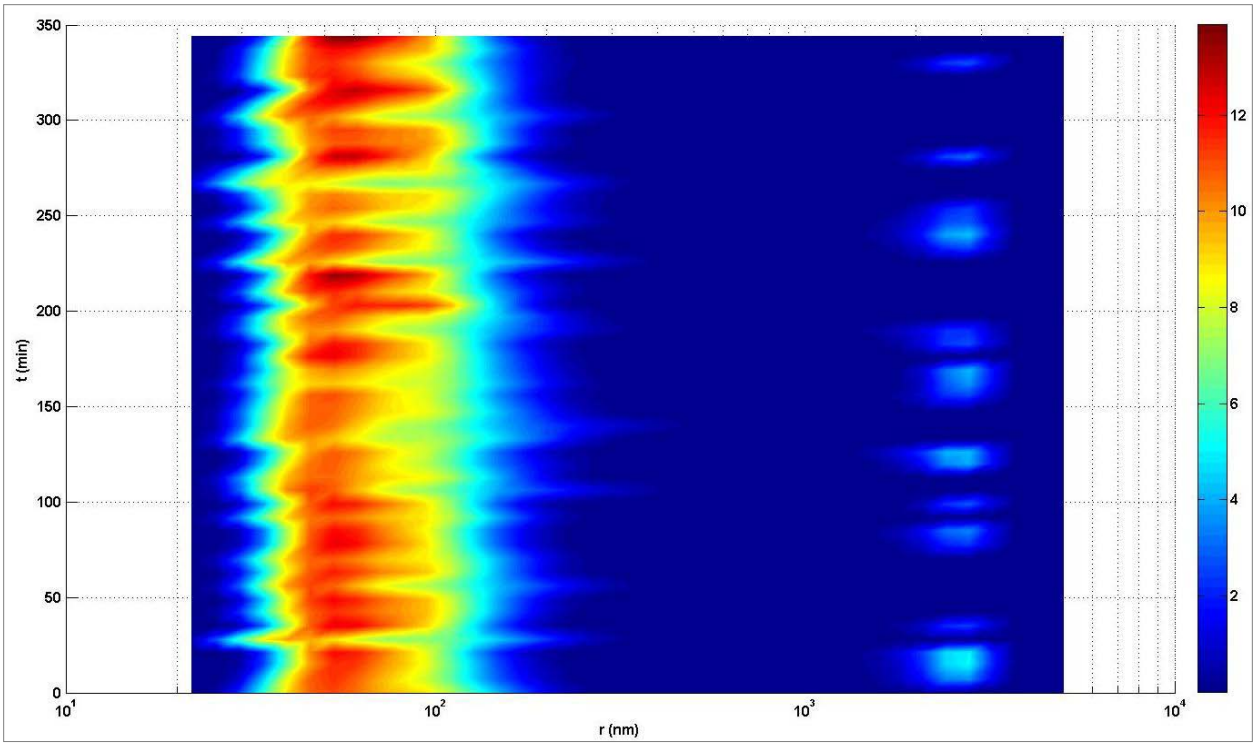

Figure 5. Color Map of Aggregates for Stability Analysis

As the size of the aggregate increases, the Brownian velocity decreases. This results in lower probability of collision between particles and aggregates and is the reason for low concentration of aggregates at higher aggregate sizes. However, the microclusters are primarily the result of collision of two or more larger nanoclusters. The growth of these aggregates cannot be sustained due to larger mass and lower mobility. Such unstable aggregates break up to form smaller and stable nanoclusters and is the reason for the appearance of microclusters only at certain time intervals during DLS measurements. The decrease in concentration of microclusters with time followed by their complete absence at the end of 350 minutes supports the fact that nanofluids are stable over long time periods with aggregate size primarily confined to nanometer size range.

5.0 DILUTE AND REGULAR NANOFLUIDS

For purposes of this discussion, 1.0 percent and 0.2 percent by volume nanofluids will be referred to as regular and dilute nanofluids, respectively. Three sets of DLS measurements were conducted on regular and dilute nanofluids. The averaged volume distribution of the clusters as a function of aggregate radius obtained using DLS measurements is shown in Figure 6.

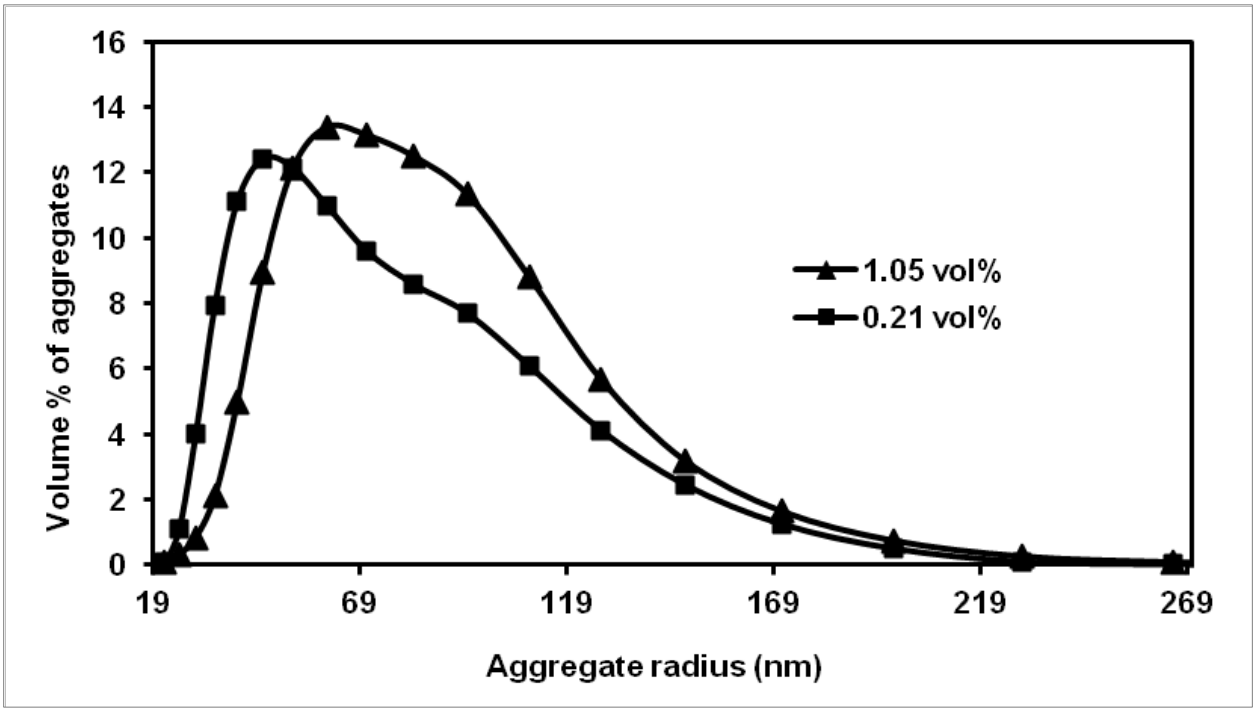

Figure 6. Aggregate Size Distribution in Dilute and Regular Nanofluids

The aggregate volume fraction for dilute nanofluid peaks at 12.4 percent at a radius of 45.64 nm. Nanoparticles in solution collide due to Brownian motion to form aggregates with a radius greater than 20 nm. With the increasing size, the velocity of the aggregates is reduced, resulting in decreased diffusion. For dilute nanofluids, the low diffusion of aggregates combined with low particle concentration results in lower collision probability and low volume fraction of aggregates above 45.64 nm. For regular nanofluids, the volume fraction peak occurs at 13.38 percent at 61.21 nm. It should also be noted that there is a higher volume fraction of aggregates

in a regular nanofluid beyond 45.64 nm compared to dilute nanofluid. In regular nanofluids, while the aggregate diffusion is lower at higher radii, the number of particles is five times higher compared to dilute nanofluids, thereby increasing the probability of collision to form larger aggregates. Thus, the majority of the smaller aggregates that were formed in a regular nanofluid collides and sticks to form larger aggregates, causing the peak to shift from 45.64 nm to 61.21 nm. The significance of this result is that with the overall increase in volume fraction and number of particles, DLCCA mechanism drives to form larger clusters at higher volume fractions. In the next few sections, this data will be applied to the aforementioned thermal conductivity models to determine the impact of aggregation on thermal conductivity. In comparing Figure 6 and Figure 7, it can be concluded that the cumulative volume percentages of smaller aggregates are higher for a dilute nanofluid as opposed to a regular nanofluid and that the higher concentrations of alumina nanoparticles leads to formation of larger clusters.

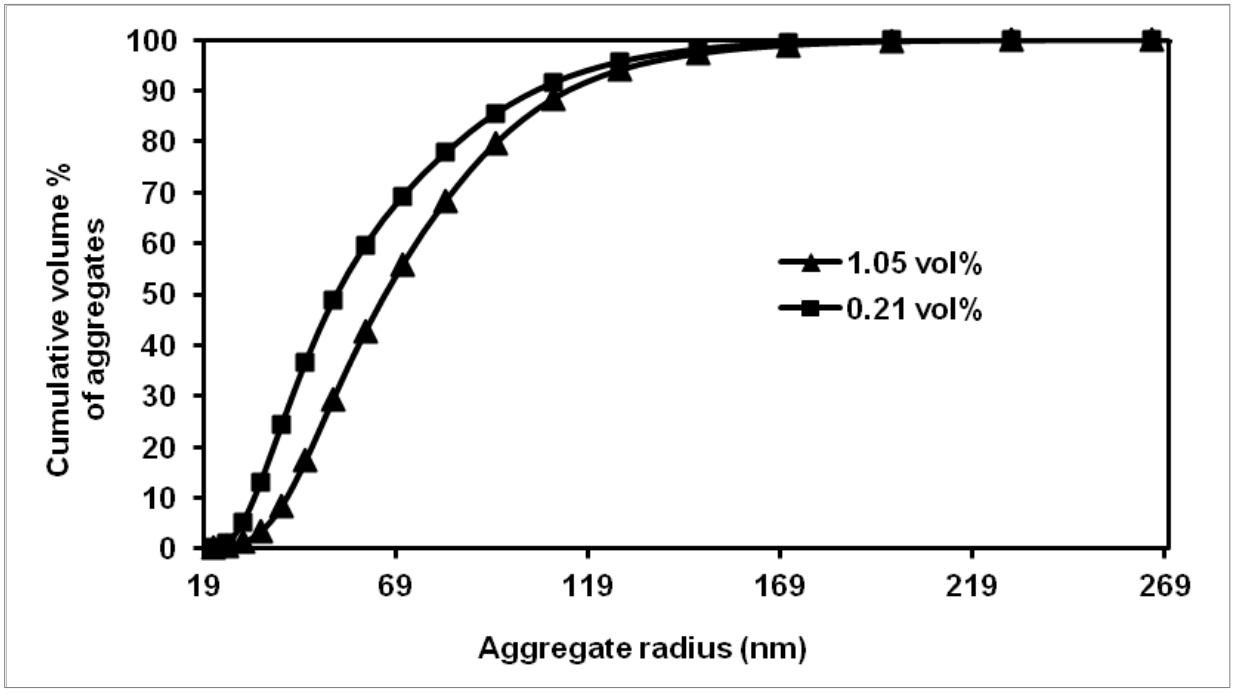

Figure 7. Cumulative Volume Fraction of Aggregates in the Nanofluid

The Maxwell model yields a thermal conductivity value of 0.6044 W/m.K and 0.6074 W/m.K for the regular and dilute nanofluids, respectively, with the respective percentage enhancements in thermal conductivities, from the base fluid, being 3 percent and 0.6 percent for the two nanofluids. The number of particles in a single aggregate can be evaluated using $N = (r_{cl}/r_a)^D$, where $D = 1.85$ for DLCCA process. Figure 8 shows that as the radius of the aggregate increases thirteen-fold, from 20 nm to 260 nm, the number of particles per aggregate increases to a maximum of 120 with the Brownian velocity dropping below 50 m/s. This decrease in velocity decreases diffusion, and thereby limits larger aggregates from further growth.

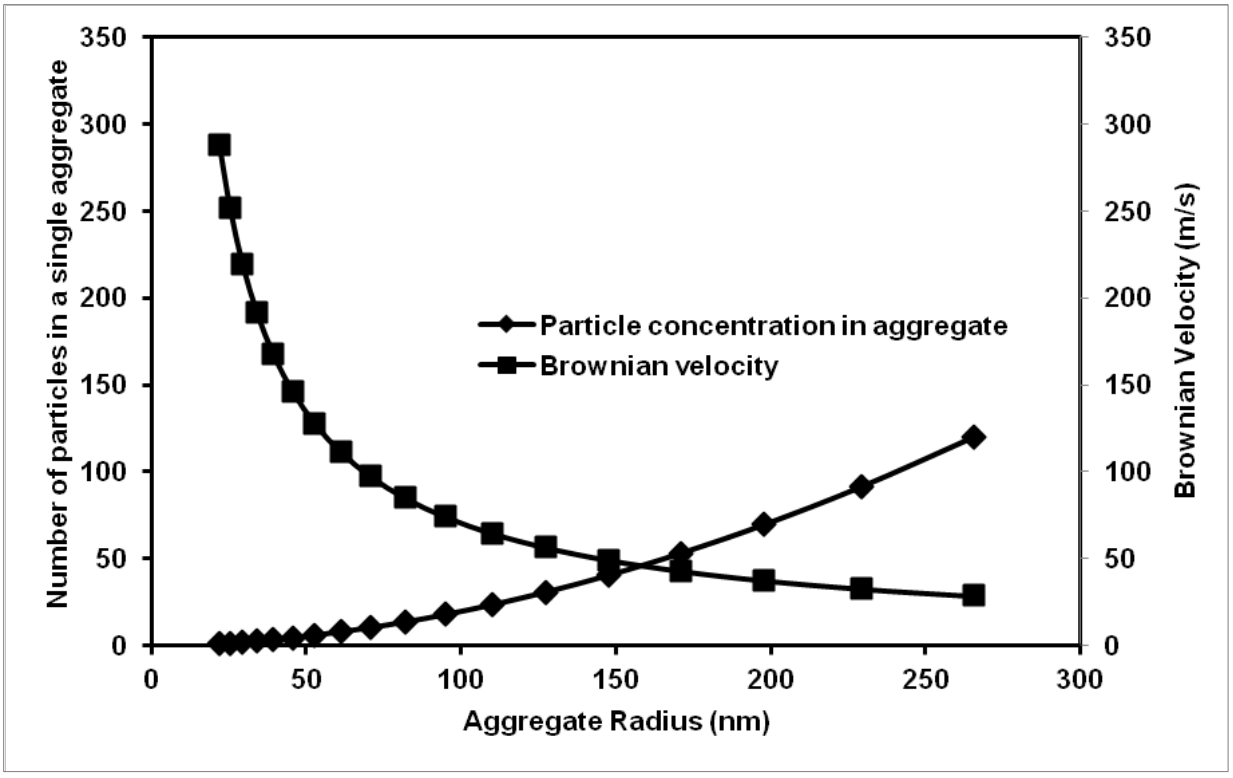

Figure 8. Particle Concentration per Aggregate and Brownian Velocity

Figure 9 shows the volume fraction of nanoparticles in a single aggregate (φ^*), as illustrated by Equations 4 and 5, and this is related to the number of particles per aggregate (N) by the relation, $\varphi^*=N(r_a/r_{cl})^3$.

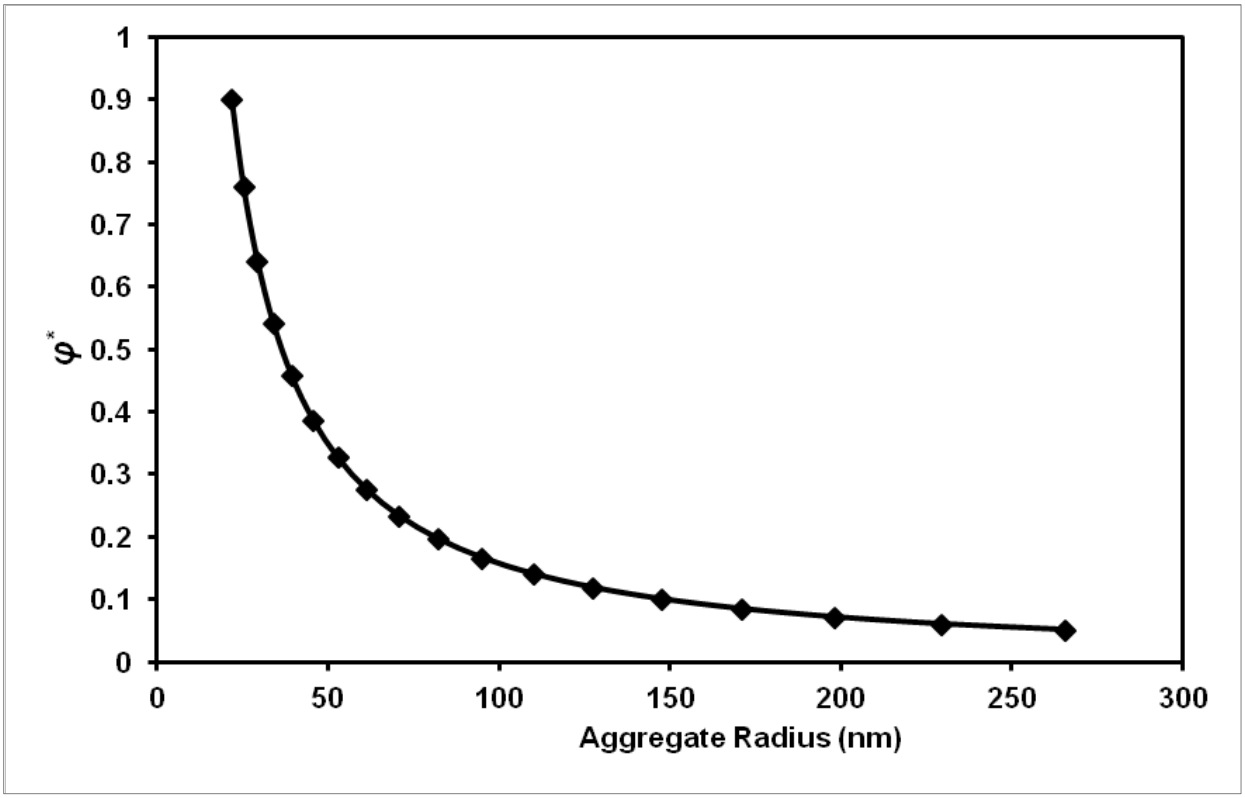

Figure 9. Volume Fraction of Nanoparticles in a Single Aggregate

While the maximum hydrodynamic radius of the aggregate is approximately 265 nm, the total number of particles at that size remains around 120 nm. This shows that with increase in hydrodynamic radius, the aggregate becomes less compact. Therefore, the hydrodynamic radius of the aggregate is a cluster of aggregated nanoparticles containing base fluid within the cluster, and the resulting percolating clusters (Prasher *et al.*, 2006) are analyzed for enhancement of the thermal conductivity of the nanofluid.

Table 1 lists the thermal conductivities of alumina nanofluids with particle concentrations at 1.05 percent and 0.21 percent that were evaluated using the Maxwell model, Fractal model, and combined Fractal and Nanolayer model. Figure 10 shows the percentage of enhancement in thermal conductivity for each of the three models relative to the base fluid.

Table 1. Model-Based Thermal Conductivities of Alumina Nanofluids

Particle Volume %	Thermal Conductivity (W/m.K)			
	Base Fluid	Alumina Nanofluid		
		Maxwell Model	Fractal Model	Fractal and Nanolayer Model
1.00	0.5868	0.6044	0.6298	0.6312
0.21	0.6038	0.6074	0.6127	0.6130

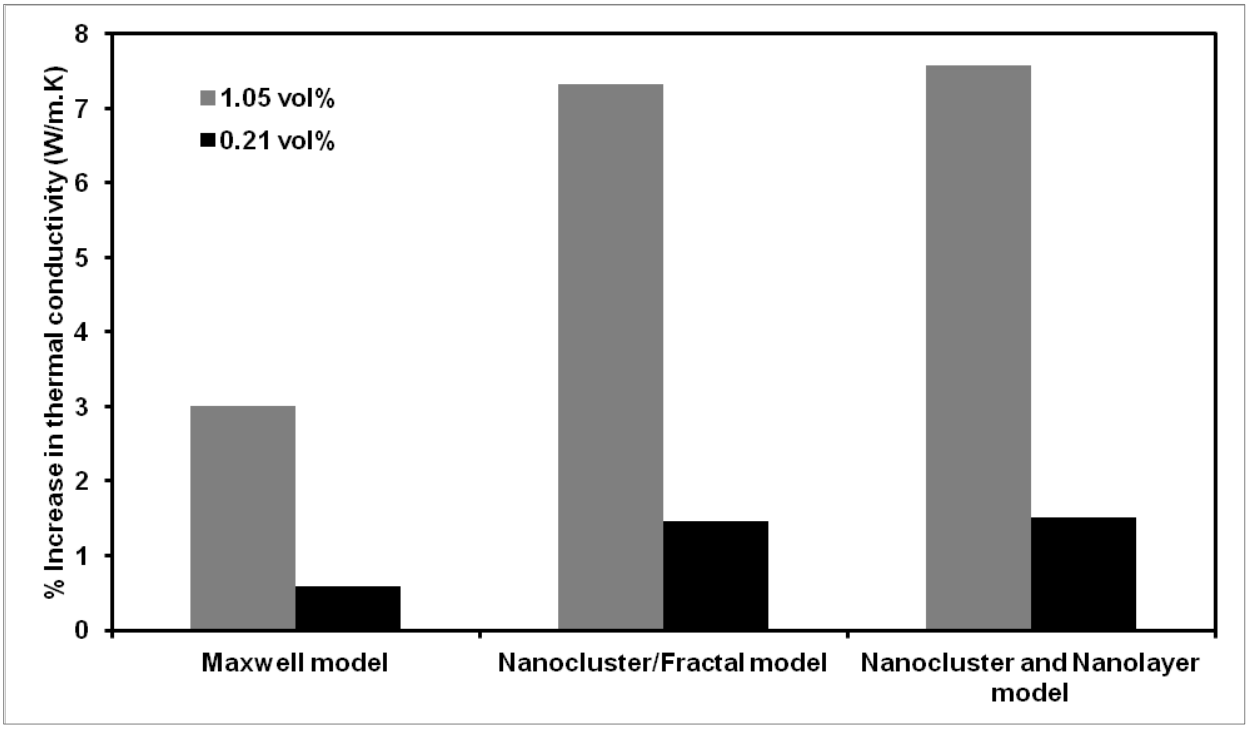

Figure 10. Thermal Conductivity Enhancements of Nanofluids

Table 2 lists the percentage of enhancement in thermal conductivity for all the models. As we move from a nanofluid containing completely dispersed nanoparticles to a nanofluid with aggregation and percolating clusters, the thermal conductivity of the clustered regular nanofluid is 2.44 times greater than a completely dispersed nanofluid. When liquid layering around percolating clusters is considered, the thermal conductivity of the regular nanofluid increases to 2.52 times greater than that of a completely dispersed nanofluid. For dilute nanofluid, thermal conductivities were enhanced 2.47 times for fluid with percolating clusters and enhanced 2.55 times for percolating clusters with liquid layering around clusters.

The results indicate that thermal conductivity increases by approximately the same amount for both dilute and regular nanofluids as we move from well-dispersed condition to percolating clusters and liquid layering around aggregates. The results also indicate that liquid layering around nanoparticle clusters does not additionally contribute to significant increases in thermal conductivity of the nanofluid. The ratio of enhancement in thermal conductivity between well-dispersed nanofluid and aggregated system with or without liquid layering is the same regardless of nanoparticle concentration, over-dilute and regular concentration regimes.

Table 2. Percentage of Enhancement in Thermal Conductivity of Alumina Nanofluids

Particle Volume %	Thermal Conductivity Enhancement (%)		
	Maxwell Model	Fractal Model	Fractal and Nanolayer Model
1.05	3.0020	7.3211	7.5698
0.21	0.5946	1.4649	1.5151

For well-dispersed nanofluid, the thermal conductivity increases by approximately five times as the nanoparticle volume concentration increases from 0.21 percent in a dilute nanofluid to 1.05 percent in a regular nanofluid. The results show that thermal conductivity increases five-fold for both the percolating cluster model and the cluster-liquid layering model as the particle concentration increases five-fold from regular to dilute nanofluid. This indicates that the linear relationship between thermal conductivity enhancement and particle concentration is well-preserved for nanofluids that are well-dispersed and for nanofluids that have percolating clusters with and without liquid layering. Thus, sensitivity to concentration is the same across different mechanisms of particle interaction in the nanofluid.

6.0 EFFECT OF VOLUME FRACTION ON THERMAL CONDUCTIVITY

Five samples with volume percent ranging from 1% to 5% were prepared and analyzed using the DLS technique to evaluate thermal conductivity as a function of nanoparticle concentration. The samples that were used for DLS measurements at TARDEC were: FL-14193-11, FL-14194-11, FL-14195-11, FL-14196-11 and FL-14197-11. The properties of the five nanofluid samples are listed in Table 3. The size distribution of aggregates in 1% to 5% by volume of alumina nanofluid is shown in Figure 11.

Table 3. Properties of Alumina Nanofluid for Volume Fraction Study

Sample Code	Mass Al_2O_3 (g)	Mass of H_2O (g)	Total Mass (g)	Mass Fraction Al_2O_3	Φ Al_2O_3	Molecular Weight (g/gmol)	Density of Fluid (kg/m^3)
FL-14193-11	1.481	39.0926	40.5736	0.0365015	0.0101322	18.5578	1028.02
FL-14194-11	2.9611	38.9629	41.924	0.0706301	0.0201207	19.1754	1055.68
FL-14195-11	4.4419	38.2292	42.6711	0.1040962	0.0304382	19.5171	1084.29
FL-14196-11	5.9202	38.1422	44.0624	0.1343594	0.0402493	20.1535	1111.53
FL-14197-11	7.4076	37.066	44.4736	0.1665617	0.0512309	20.3416	1142.06

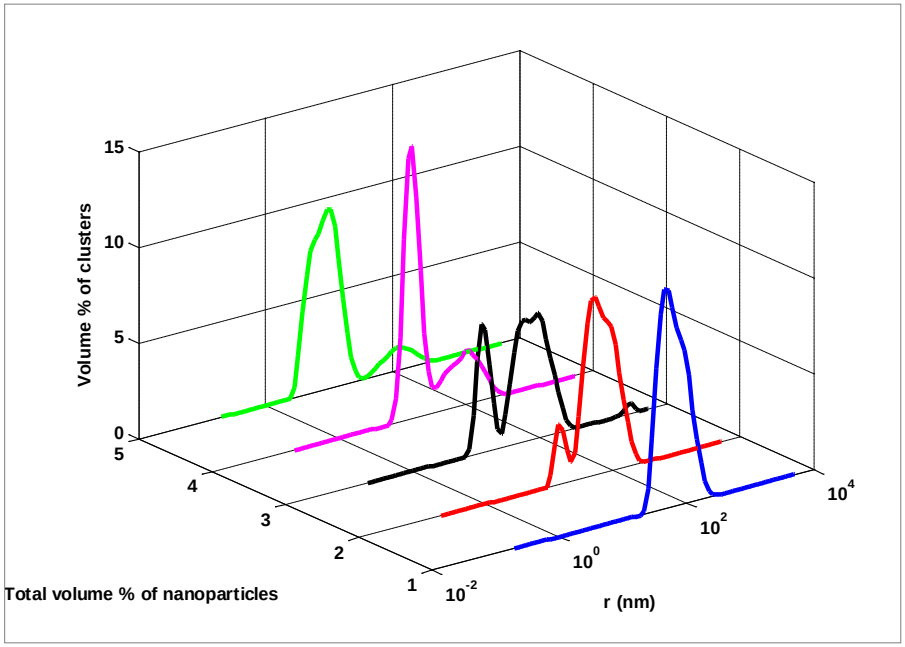

Figure 11. Size Distribution of Aggregates in 1% to 5% by Volume of Alumina Nanofluid

In Figure 11, it should be noted that 99% of their aggregates in all the nanofluid samples have a size less than 500 nm. The only exception occurs at 3% by volume concentration where microcluster concentration is less than 1% of the total volume of clusters. The formation of microclusters at this concentration is an exception and can be attributed to conditions similar to that shown in Figure 5, where the microclusters formed are unstable, less than 1% of the total volume of clusters and breaks up to form smaller nanoclusters. The molecular weight and density of the nanofluids were used in thermal conductivity models (equations 2 to 11) to compute the effective thermal conductivity of the nanofluid. The percentage of enhancements in thermal conductivity based on these models are summarized in Table 4. The percentage of enhancements in thermal conductivity as a function of total volume percentage of nanoparticles in the nanofluid samples is shown in Figure 12.

Table 4. Summary of Enhancement in Thermal Conductivity Values

Φ	Percentage Enhancement in Thermal Conductivity (W/m.K)		
	Maxwell Model	Fractal Model	Modified Fractal Model
1.0132	2.8896	7.0589	7.5602
2.0120	5.7932	13.997	14.464
3.0438	8.8514	21.145	21.842
4.0249	11.816	27.922	28.837
5.1230	15.204	35.485	36.630

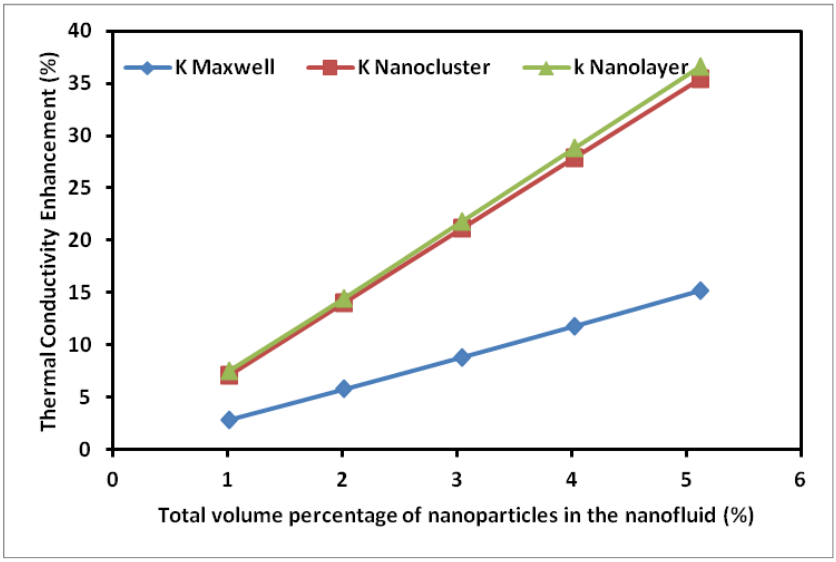

Figure 12. Thermal Conductivity Enhancement versus Total Volume Percent of Nanoparticles

The models predict an overall enhancement in thermal conductivity of up to 35% at 5% by volume of alumina nanoparticle concentration. These values are well in agreement with the comprehensive literature review published by Özerniç et al., 2009. This literature review shows a maximum of 32.4% enhancement in thermal conductivity with alumina water nanofluids with concentrations from 1.30% to 4.30% percent by volume. Therefore, the thermal conductivity models based on aggregation and interfacial layer formation have been validated.

7.0 CONCLUSIONS AND FUTURE RESEARCH

The research study consisted of three main phases. Phase-I was focused on stability analysis of 1% by volume alumina nanofluid solution. The experiment determined the size range of aggregates in the nanofluid solution due to Brownian motion of particles, using the DLA technique. It was concluded that the aggregate formation was restricted primarily to the nanometer size range. The microclusters that formed at certain time intervals were unstable and resulted in the formation of individual nanoclusters. It was also inferred that the total volume percent of microclusters during the entire duration of stability analysis was less than 1%.

Phase-II of this research study focused on dilute and regular nanofluids with 0.21% and 1.05% by volume concentration of alumina nanoparticles. The nanofluids were characterized using DLS measurements to obtain percentage volume distribution as a function of hydrodynamic aggregate radius. It was concluded that the lack of a sufficient number of nanoparticles at dilute concentration reduced the collision probability and growth of larger percolating clusters. The DLS results were used to compute the effective thermal conductivity of nanofluids using percolating clusters and liquid layers around aggregates, and compared it to a well-dispersed alumina nanofluid. It was concluded that the thermal conductivities of both dilute and regular nanofluids increased approximately 2.5 fold compared to a well-dispersed nanofluid, and that the contribution of liquid layering to enhancement in thermal conductivity is negligible for all practical purposes. It was also concluded that a near-linear relationship between concentration and thermal conductivity is preserved for nanofluids that were well-dispersed, and with percolating clusters and liquid layering. Thus, agglomeration with percolating clusters accounted for a significant increase in thermal conductivity of nanofluids across dilute and regular concentration regimes.

Phase-III of the nanofluids research was focused on examining the relationship between total volume fraction of nanoparticles and the percentage of enhancement in thermal conductivity using the three thermal conductivity models. It was again concluded that aggregation played a major role in thermal conductivity enhancement and that a maximum of 35% enhancement was estimated at 5% volume fraction of alumina nanoparticles. The computed values of thermal

conductivity closely match with experimental values published in the literature. Therefore, the DLS measurements of nanofluids have been validated based on the thermal conductivity models.

Based on the above conclusions, agglomeration of nanoparticles was determined to be a dominant factor in the overall thermal conductivity enhancement of nanofluids. By manipulating the size of the percolating clusters and volume distribution, nanofluids can be engineered for applications that require specific thermal conductivities for use in ground vehicles. Future research work in the area of nanofluids will focus on aggregation characteristics of nanoparticles in fluid due to sonication time, power and nanoparticle concentration. The aggregation characteristics will be investigated using the Scanning Electron Microscopy (SEM) technique.

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